

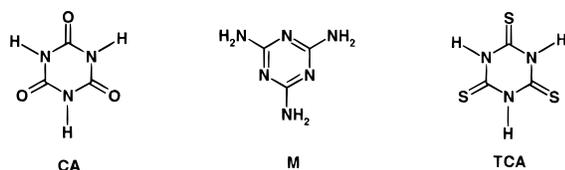
## Hydrothermal Synthesis of Organic Channel Structures: 1:1 Hydrogen-Bonded Adducts of Melamine with Cyanuric and Trithiocyanuric Acids

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Whitesides and co-workers<sup>1</sup> have extensively cited the 1:1 hydrogen-bonded adduct between cyanuric acid (CA) and melamine (M)-forming rosettes, as an outstanding case of noncovalent synthesis. The hydrogen-bonded CA·M lattice is the template on which these workers based the design of a family of self-assembled hydrogen-bonded aggregates, stable in solution.<sup>2,3</sup> The CA·M adduct is expected to form a hexagonal network through the formation of hydrogen bonds between the two molecules, but the structure has not been established by single-crystal X-ray crystallography.<sup>3</sup> The crystal structure of CA·M·3HCl reported by Wang et al.<sup>4</sup> reveals one-dimensional tapes rather than the rosette structure. The difficulty in growing crystals of the CA·M adduct is partly because CA and M are both highly hydrogen-bonded solids melting at high temperatures, with limited solubility in most organic solvents. Mixtures of CA and M in water or alcohol solution give precipitates containing the adduct, but do not yield crystals suitable for X-ray crystallography.<sup>1,3</sup> We felt that to obtain single crystals of the CA·M adduct, it may be necessary to employ more drastic conditions than normally employed. We have, therefore, made use of hydrothermal conditions,<sup>5</sup> commonly employed in the synthesis of quartz, zeolites, and inorganic open-frame structures, to obtain the crystals of the 1:1 adduct. We have indeed been able to obtain good crystals of the 1:1 CA·M adduct by this means. Crystals of the 1:1 adduct of trithiocyanuric acid (TCA) and M could also be



prepared hydrothermally. We report the structures of both of these fascinating adducts of M in this paper.

The procedure for preparing the crystals of the CA·M adduct was as follows. Aqueous solutions of cyanuric acid (0.1 mmol) and melamine, (0.1 mmol) were mixed in a Teflon flask, and the mixture (15 mL) was kept in a stainless steel bomb. The bomb was sealed and maintained in a furnace at 180 °C. Rectangular platelike crystals of good quality separated from the solution, upon cooling the bomb to room temperature over a period of 4 h. These crystals were used for collecting intensity data on the single-crystal

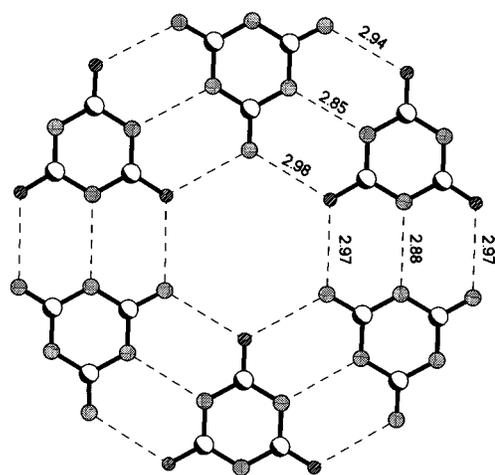
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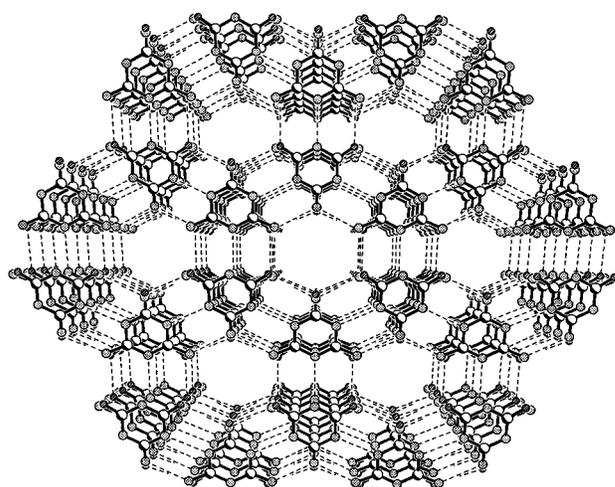
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(a)



(b)

**Figure 1.** (a) A rosette formed between cyanuric acid (CA) and Melamine (M) in the adduct of CA·M with a cavity diameter of approximately 4 Å. Dashed lines represent intermolecular hydrogen bonds. (b) Three-dimensional arrangement of the CA·M adduct forming channels along the crystallographic *c*-axis.

X-ray diffractometer. Crystals of the 1:1 TCA·M adduct were obtained by a similar procedure except that the temperature was maintained at 100 °C.<sup>6</sup>

The 1:1 CA·M adduct<sup>7</sup> has an asymmetric unit consisting of superimposed CA and M molecules.<sup>8</sup> Packing analysis shows that

(6) TCA decomposed when the temperature was maintained at 180 °C as in the case of CA.

(7) Crystal data for the CA·M adduct: (C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>O<sub>3</sub>):(C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>), *M* = 255.22, crystal dimensions, 0.3 × 0.2 × 0.2 mm, monoclinic, space group, *C2/m*, *a* = 14.853(2) Å, *b* = 9.641(2) Å, *c* = 3.581(1) Å, β = 92.26(1)°, *V* = 512.4(2) Å<sup>3</sup>, *Z* = 2, ρ<sub>calcd</sub> = 1.654, μ(Mo Kα) = 0.136 mm<sup>-1</sup>, *F*(000) = 264, λ = 0.710 73 Å, Smart CCD area detector, Siemens, ω-2θ scan, 2° < θ < 24° (-16 ≤ *h* ≤ 14, -8 ≤ *k* ≤ 10, -3 ≤ *l* ≤ 3), 1095 total reflections, 395 independent reflections which were used for refinement. The structure was solved by direct methods (SHELXTL-PLUS) and refined by full-matrix least squares on *F*<sup>2</sup> (SHELX-93; G. M. Sheldrick, Gottingen, 1993) to *R*<sub>1</sub> = 0.056 and *wR*<sub>2</sub> = 0.141. Residual density, min/max -0.495/0.393 e·Å<sup>-3</sup>. Hydrogen atoms were not included in the refinement, but including the hydrogen atoms in the calculated positions improves the *R*-factor by 1%.

(8) The best stacking arrangement was one with alternating CA and M molecules (with 50% occupation each), as established by the low *R*-factor and also by energy calculations using the MOPAC program. The least stable arrangement is the one with CA on top of another CA, as one would expect.

CA and M are held together by N—H···O and N—H···N hydrogen bonds yielding the hexamer (rosette) shown in Figure 1a. The interatomic N···O and N···N distances corresponding to N—H···O and N—H···N bonds are in the range of 2.94–2.98 and 2.85–2.88 Å, respectively. The hexamers are arranged in two dimensions to form planar sheets, the structure being exactly as predicted by Whitesides.<sup>1</sup> A significant feature is that the planar sheets are stacked in three dimensions<sup>8</sup> to give channels with a diameter of 4 Å (Figure 1b). These channels are comparable to the cavities in cryptands.<sup>9</sup>

Crystal structure determination of the TCA·M adduct<sup>10</sup> reveals that it has features similar to those of the CA·M adduct, except that the N—H···O hydrogen bonds are replaced by the N—H···S hydrogen bonds as shown in Figure 2a. The N···S and N···N distances corresponding to N—H···S and N—H···N bonds are in the range of 2.96–2.99 and 2.86–2.88 Å, respectively. The sheets are stacked in a three-dimensional channel arrangement as depicted in Figure 2b. The diameter of the channel is approximately 4 Å here as well.

The present study illustrates the efficacy of the hydrothermal method to prepare crystals of organic materials in certain special situations, as in the present case where the compounds are highly hydrogen-bonded (with limited solubility in common solvents) and give precipitates when mixed in water.<sup>11</sup>

It is noteworthy that the adducts of M with CA and TCA constitute members of a rare class of organic solids containing channels.<sup>12</sup> Trimesic acid is a good example of a system forming hexagonal channels.<sup>13</sup> The other example of such a solid is the adduct of TCA with 4,4'-bipyridyl.<sup>14</sup> Experiments to explore whether the channels in the CA·M adduct can be filled by cations and other species are in progress.

CA on top of M is more stable by 37 kcal mol<sup>-1</sup> relative to CA on CA. The packing coefficient of the CA·M adduct calculated by using Cerius is 67.5%.

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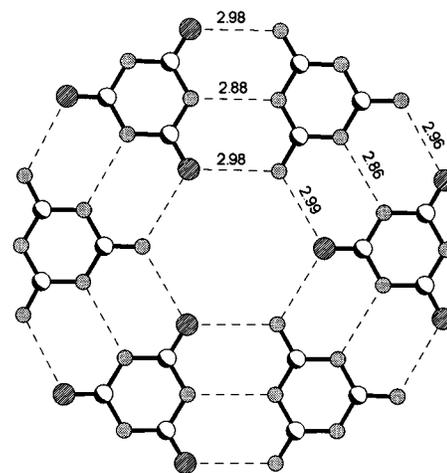
(10) Crystal data for the TCA·M adduct: (C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>S<sub>3</sub>):(C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>) M = 303.39, crystal dimensions, 0.3 × 0.25 × 0.35 mm, monoclinic, space group, C2/m, a = 14.862(3) Å, b = 9.650(2) Å, c = 3.588(1) Å, β = 92.32(1)°, V = 514.2(2) Å<sup>3</sup>, Z = 2, ρ<sub>calcd</sub> = 1.901, μ(Mo Kα) = 0.716 mm<sup>-1</sup>, F(000) = 294, λ = 0.710 73 Å, Smart CCD area detector, Siemens, ω–2θ scan, 2° < θ < 24° (–13 ≤ h ≤ 16, –10 ≤ k ≤ 10, –3 ≤ l ≤ 3), 1091 total reflections, 397 independent reflections which were used for refinement. The structure was solved by direct methods (SHELXTL-PLUS) and refined by full-matrix least squares on F<sup>2</sup> (SHELX-93; G. M. Sheldrick, Gottingen, 1993) to R1 = 0.062 and wR2 = 0.134. Residual density, min/max –0.396/0.487e<sup>-3</sup>. Hydrogen atoms were not included in the refinement, but including the hydrogen atoms in the calculated positions improves the R-factor by 1%. The best stacking arrangement is TCA on top of M (see (8) for details). The packing coefficient of the adduct is 74.6% as calculated from Cerius.

(11) The powder X-ray diffraction pattern of the CA·M adduct simulated on the basis of structure found by us agrees with the experimental powder pattern of the precipitate or of the polycrystalline sample.

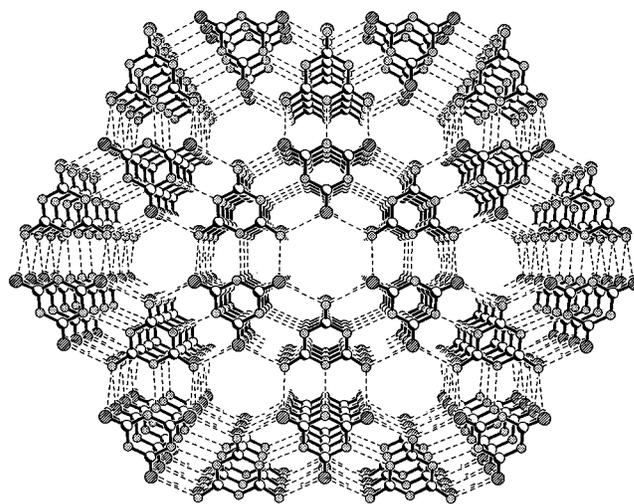
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(a)



(b)

**Figure 2.** (a) Hexagonal network (rosette) formed between trithiocyanuric acid (TCA) and Melamine (M) in the adduct of TCA·M with a cavity diameter of approximately 4 Å. (b) Three-dimensional arrangement of the TCA·M adduct forming channels along crystallographic *c*-axis.

**Supporting Information Available:** Two figures (ORTEP drawings of the adducts CA·M and TCA·M with labeling scheme) and 6 tables containing general crystallographic information, fractional coordinates of non-hydrogen atoms, list of bond lengths and angles, and anisotropic displacement parameters (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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